Structural Analysis of Rust Layer on Low-Alloy Steels Exposed for 17 Years Using X-Ray and Mössbauer Spectroscopy

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Abstract: We have examined the rust layers formed on carbon and weathering steels exposed for 17 years in various atmospheric environments with different air-borne sea-salt content by using the X-ray diffraction and the Mössbauer spectroscopies. It was found that the rust layers mainly consisted of the superparamagnetic ultra-fine Cr-goethite, the X-ray detectable Cr-goethite and β-FeOOH. Mass fraction of β-FeOOH increased with increasing corrosion loss of the steels in the higher salt-content environment. However, mass fractions of both of the ultra-fine Cr-goethite and the X-ray detectable Cr-goethite showed their maximum at 0.04md. Increase in the mass fraction of β-FeOOH and decrease in that of the goethite type phase in higher atmospheric salt content caused the lower protective ability of the rust layer against the atmospheric corrosion. In conclusion, it was pointed out that the rust transformation route with time towards the goethite type phase or β-FeOOH is extremely important for discussing the protective ability of the rust layer in the environment with higher salt content.

Key words: Weathering steel, Rust layer, Atmospheric corrosion, X-ray diffraction spectroscopy, Mössbauer spectroscopy

1. INTRODUCTION

A rust layer formed on a low-alloy steel surface is generally considered to be responsible for protection of the steels against corrosives in atmospheric environment. It is well known that the rust layer, so-called "protective" rust layer, formed on a weathering steel which contains a small amount of Cr, P and Cu has strong protective ability for atmospheric corrosion of the steel. The study of the rust layers formed on the steels and their control have become a principal theme in the field of atmospheric corrosion, since the rust layers give certain beneficial effects for prevention of degradation of the steels.

Weathering steel possesses high corrosion resistance, approximately twice as good as carbon steels, and therefore has been widely used as a structural material in an atmospheric corrosion environment. However, there has been a problem when the weathering steels are used as a structural material, because the protective rust layer is usually formed spontaneously after more than 10 years exposure. Until the protective ability of the rust layer emerges, the corrosion rate of the weathering steel is not considerable low and initial unprotective rust contaminates surfaces of itself and other environing materials. In addition, the protective rust layer cannot form in the coastal environment where the amount of air-borne sea-salt particle is relatively high. These are significant problems to reduce maintenance task for structures made of the weathering steel. Public Works Research Institute of the ministry of construction in Japan reported the necessity of development of steel materials with long-term life, which enable us to obtain steel structures with minimum maintenance.

According to the recent understanding of the protective rust layer [1,2], the main constituent of the rust layers is changed with the exposure period to atmospheric environment with a low air-borne salt content from γ-FeOOH, lepidocrocite, (less than a few years), via the X-ray amorphous substance (several years), to α-FeOOH, goethite, type phase (decades). The corrosion rate of the weathering steel decreases with this long-term phase transformation of the rust layer. The protective rust layer possesses the structure of α-(Fe₆₋₇Crₓ)O₉H₂Cr-goethite, which might be formed due to concentration of Cr in the rust layer after long-term exposure.

It is said that the Cr content in the Cr-goethite increases gradually with reaching the rust/steel interface [3]. This increase in the Cr content and resultant aggregation of smaller crystals lead a denser Cr-goethite rust layer which provides higher protective ability for atmospheric corrosives. It is also pointed out that the Cr-goethite possesses the cation selective ability. Therefore, the protective rust layer of the Cr-goethite impedes the penetration of aggressive corrosive anions such as Cl⁻ and SO₄²⁻, as well as its densely aggregated structure which provides the resistance against a corrosive penetration [3].

Even if the above mentioned protective ability of the Cr-goethite emerges in a low salt-concentration environment, it is very important to answer why the protective rust layer does not form in the atmospheric environment with a higher salt-content. In this paper, we have examined rust layers formed on low-alloy steels exposed for 17 years in various atmospheric environments with different salt content by using the X-ray diffraction and the Mössbauer spectroscopies.
2. EXPERIMENTAL PROCEDURE

2.1. Rust Layer
The rust layers examined were formed on low-alloy steel panels with the dimensions of 100mm" × 150mm × 8mm exposed systematically to the atmosphere underneath the girders of 5 bridges for 17 years in the main island of Japan. This exposure test has been done by Public Works Research Institute, Japan Association of Steel Bridge Construction and The Kozai Club. Table 1 indicates the environmental conditions of the exposure sites, where the salt content in the atmosphere varies between 0.005-0.093 mg NaCl/100cm^2/day (mdd). Steels A-E shown in Table 2 were exposed at all the sites. Steel A is a mild steel. Steels B and C correspond to conventional weathering steels. Steels D and E are designed for higher resistance to atmospheric corrosion by adding larger amount of phosphorous. All the steel panels were positioned horizontally under the bridge girder. Fig.1 shows the corrosion loss per single side of Steel B, the typical weathering steel, as a function of exposure time. It is obvious that the corrosion loss increases with increasing the salt content. Other steels also show the same behavior, as shown in Fig.2 which indicates the corrosion loss of each steel as a function of the salt content. The corrosion loss of Steel A was much higher than those of other steels. This means that the weathering steels possessed higher corrosion resistance than the plain carbon steel. Thickness of rust layer formed were approximately 100-300 μm.

Table 1. Environmental conditions of the exposure sites

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Bridge name</th>
<th>Exposure site</th>
<th>Environmental condition</th>
<th>Salt content in atmosphere (mg/100cm^2/d)</th>
<th>SO2 content in atmosphere (mg/100cm^2/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>07</td>
<td>Natogawa - Hachioji</td>
<td>Sendai</td>
<td>Urban(A)</td>
<td>0.029</td>
<td>0.026</td>
</tr>
<tr>
<td>08</td>
<td>Ominesawa - Basho</td>
<td>Mikurito</td>
<td>Mountainous</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>10</td>
<td>Ebiga - Ohashi</td>
<td>Funabashi</td>
<td>Coastal</td>
<td>0.093</td>
<td>0.140</td>
</tr>
<tr>
<td>18</td>
<td>Yoikasugi - Hanashi</td>
<td>Nagoya</td>
<td>Urban(B)</td>
<td>0.016</td>
<td>0.268</td>
</tr>
<tr>
<td>19</td>
<td>Yokkaichi - Kohakyo</td>
<td>Yokkaichi</td>
<td>Industrial</td>
<td>0.041</td>
<td>0.109</td>
</tr>
</tbody>
</table>

Table 2. Chemical compositions of the steels. (mass%)

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>Ti</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.17</td>
<td>0.32</td>
<td>1.39</td>
<td>0.016</td>
<td>0.012</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.12</td>
<td>0.39</td>
<td>0.90</td>
<td>0.008</td>
<td>0.006</td>
<td>0.36</td>
<td>0.61</td>
<td>0.22</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.11</td>
<td>0.20</td>
<td>0.88</td>
<td>0.014</td>
<td>0.010</td>
<td>0.30</td>
<td>0.51</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>0.06</td>
<td>0.38</td>
<td>1.28</td>
<td>0.091</td>
<td>0.006</td>
<td>0.34</td>
<td>0.35</td>
<td>0.30</td>
<td>-</td>
<td>0.015</td>
<td>0.05</td>
</tr>
<tr>
<td>E</td>
<td>0.06</td>
<td>0.53</td>
<td>1.42</td>
<td>0.085</td>
<td>0.004</td>
<td>0.32</td>
<td>-</td>
<td>0.02</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2. X-ray Diffraction Spectroscopy
Rust samples were removed from the skyward surface by a razor until the steel surface appeared, and then ground into powder. The powdered rust samples were desiccated for a week in advance of the analyses. The powdered samples were characterized by means of the X-ray diffraction and the Mössbauer spectroscopies. The X-ray diffraction experiments were done employing a Co target. The quantitative determination of the rust constituents comprising goethite, γ-FeOOH, β-FeOOH, FeO, and the X-ray amorphous substances was carried out by measuring the diffraction intensities and comparing that of ZnO powder which had been mixed with the rust samples as an internal standard [4]. The remainder other than the above X-ray detectable crystalline constituents were defined as the X-ray amorphous substances in this quantifying estimation since the amounts of other crystalline materials and air-borne dusts might be very small.

2.3. Mössbauer Spectroscopy
In order to separately identify the iron oxides which were either superparamagnetic at 300K or which magnetically ordered between 300 and 77K, the transmission Mössbauer spectroscopy was used. This can distinguish the size difference of the rust crystals making up each oxide phase, by measuring the changes in the hyperfine...
magnetic fields and the temperature dependence of the superparamagnetic relaxation. The rust samples were mixed with BN powder, ten times the rust weight, and pressed into a 1cm diameter tablet. The Mössbauer spectra were recorded using a 20mCi²⁷Co in rhodium source at room temperature 300K and 77K in a liquid nitrogen cooled cryostat. A commercial proportional counter filled with the mixture of xenon and carbon dioxide gases was used. Relative mass fraction of each rust constituent with the mass of \( m_a \) was estimated from the relative Mössbauer subsectral area, \( A_s \), by equation (1) with considering the molecular weight, \( M_s \), the relative recoilless fraction, \( F_r \), [5] and the number of iron atoms per formula unit, \( N_s \), of each rust constituent.

\[
\frac{m_s}{m_a} = \frac{A_s}{M_s} \cdot F_r \cdot N_s / \frac{A_s}{M_s} \cdot F_r \cdot N_s
\]

where the subscripts a and b indicate rust constituents a and b, respectively.

3. RESULTS

3.1. X-ray Diffraction Spectra

The X-ray diffraction spectra of the rust samples indicated that the X-ray detectable rust constituents were goethite, \( \beta\)-FeOOH and small amount of \( \gamma\)-FeOOH and Fe₃O₄. Total amount of \( \gamma\)-FeOOH and Fe₃O₄ was less than a few percent. In addition, after the quantitative determination, it was shown that the rust layers contained a large amount of the X-ray amorphous substance.

The mass fraction of goethite type phase is shown in Fig.3 as a function of the salt content in the atmosphere. Until 0.04mdd, the mass fraction of goethite type phase increases with the salt content in the atmosphere. However, the mass fraction decreases in the region over 0.04mdd. On the other hand, \( \beta\)-FeOOH increases with the salt content, as shown in Fig.4. It should be noted that the mass fraction of \( \beta\)-FeOOH does not change so much in the range between 0.02-0.04 mdd. This variation in the mass fraction of \( \beta\)-FeOOH is vary similar to the salt-content dependence of the corrosion loss of each steel. Thus, it seems that the corrosion loss is related to the mass fraction of \( \beta\)-FeOOH.

3.2. Mössbauer Spectra

The Mössbauer spectra of the rust samples formed on Steel B are shown in Fig.5. The 300K spectra show the presence of the quadrupole splitting showing a doublet with the subsectral area of about 70% of total spectral area. This doublet might be attributed to the superparamagnetic components of goethite [5], \( \gamma\)-FeOOH and \( \beta\)-FeOOH. As was pointed out above, \( \gamma\)-FeOOH does not contribute this doublet so much because the X-ray diffraction confirmed that only a very small amount of \( \gamma\)-FeOOH was present in the rust layer. In addition, \( \beta\)-FeOOH was detected less than about 10%, depending on the salt content, from the X-ray diffraction spectroscopy. Thus, most of the doublet corresponds to the superparamagnetic goethite, la-

Fig.3 Mass fraction of rust constituent with goethite type phase, \( \alpha_{\chi} \), as a function of the salt content in the atmosphere, evaluated by X-ray diffraction.

Fig.4 Mass fraction of rust constituent with \( \beta\)-FeOOH structure, \( \beta_{\chi} \), as a function of salt content in the atmosphere, evaluated by X-ray diffraction.

than 15nm and therefore be difficult to be detected by the X-ray diffraction spectroscopy. The sextet of the magnetic splitting due to the magnetic goethite [5] with the crystal size more than 15nm was also recorded. This crystal size of the magnetic goethite can be large enough to be detected by the X-ray diffraction spectroscopy.

The Mössbauer spectra recorded at 77K revealed a significant increase in the amount of magnetically ordered ferric oxhydroxides. The broad sextet now made up more than 80% of the low temperature spectral area. This increase in the magnetically ordered component, compared to the 300K spectrum, was attributed to the presence of a large amount of the superparamagnetic goethite, labeled S1-goethite, with the crystal size between 8-15nm. The remaining doublet at 77K may contain \( \gamma\)-FeOOH as identified by the X-ray diffraction and the superparamagnetic goethite, labeled S2-goethite, having crystal size less than 8nm. Therefore, the rust layers mainly consisted of the superparamagnetic goe-
Fig. 5 Mössbauer spectra of the rust layer formed on Steel B exposed at the atmosphere with the salt content of 0.005 (a), 0.041 (b) and 0.093 (c) mdd.

Fig. 6 Mass fractions of the ultra-fine Cr-goethite (Cr-UFG: crystal size <15nm), the Cr-goethite (>15nm) and β-FeOOH on the surface of Steel B as a function of the salt content in the atmosphere, evaluated by transmission Mössbauer spectroscopy.
thite, the X-ray detectable goethite, $\beta$-FeOOH, and very small amount of $\gamma$-FeOOH and FeO. Because the crystal size is very small less than 15nm, the superparamagnetic goethite is referred to in the remainder of this paper as the ultra-fine goethite (UFG). It has been pointed out that the rust layers of the weathering steels contained Cr concentrating especially in the inner layer of the rust [6]. Therefore, as was pointed out previously in the other rust layer on a weathering steel, it can be said that the UFG and the X-ray detectable goethite are the ultra-fine Cr-goethite (Cr-UFG) and the Cr-goethite, respectively. The hyperfine parameters [7] of the Cr-UFG and the X-ray detectable Cr-goethite were consistently fit to the Mössbauer spectra of the rust layers.

The fit of the hyperfine parameters [7] of iron oxides and oxyhydroxides to the Mössbauer spectra of the rust samples revealed the mass fraction of each oxyhydroxide. Figure 6 shows the mass fractions of the Cr-UFG, the Cr-goethite and $\beta$-FeOOH in the rust layers on Steel B as a function of the salt content in the atmosphere. In the range of low salt content, the rust layers were composed mainly of the Cr-UFG. About 20% of the Cr-goethite was also present. The fact that the mass fractions of both the Cr-UFG and the Cr-goethite showed their maximum at 0.04mdd. The Cr-UFG and the Cr-goethite decreased and $\beta$-FeOOH increased in the higher salt content. These variations of the mass fractions of the Cr-goethite and $\beta$-FeOOH estimated by the Mössbauer spectroscopy agree well with the results obtained by the X-ray diffraction spectroscopy being shown in Figs.3 and 4.

4. DISCUSSION

4.1. Rust Constituents and Protective Ability

It was calculated from Fig.6 that the amount of the Cr-UFG is 3-4 times as much as that of the Cr-goethite. Because the Cr-goethite is the X-ray detectable goethite and its mass fraction in the rust layer was 10-30% (Fig.3), the total amount of the Cr-UFG, the Cr-goethite and $\beta$-FeOOH is estimated to be close to 100%. This means that most of the X-ray amorphous substance is composed of the Cr-UFG.

It can be recognized by comparing the salt-content dependences of the corrosion loss (Fig.2) and those of the mass fractions of $\beta$-FeOOH (Figs.4 and 6) that the corrosion loss was closely related to the mass fraction of $\beta$-FeOOH. The fact that the corrosion loss did not increase so much in the range between about 0.02-0.04mdd can be interpreted by the results that the mass fraction of the goethite type phase increases and that of $\beta$-FeOOH does not change so much with the salt content at this range of the salt content. The corrosion loss steeply increased when the mass fraction of $\beta$-FeOOH increased in the higher salt content.

Figure 7 shows the relationship between the corrosion loss and the mass fraction of $\beta$-FeOOH evaluated by the X-ray diffraction spectroscopy. The corrosion loss increased with increasing the amount of $\beta$-FeOOH. Especially the increase rate of the corrosion loss of Steel A was considerably higher than that of the weathering steels. This means that the protective ability of the rust layer on the mild steel was inferior to that of the weathering steels.

In conclusion, it can be said that increase in the mass fraction of $\beta$-FeOOH and decrease in that of the goethite type phase, especially decrease in the mass fraction of the Cr-UFG as can be seen in Fig.6, in the higher salt content cause the lower protective ability of the rust layer against the atmospheric corrosion.

Fig.7 Corrosion loss of steel panels as a function of the amount of $\beta$-FeOOH in the rust layers.

4.2. Rust Phase Transformation

Recently, it was shown that the main constituent of the rust layer formed on a weathering steel which contains Cr is changed from $\gamma$-FeOOH to the Cr-goethite during long-term atmospheric corrosion in a low salt-content environment [1,2]. However, the rust phase transformation during long-term exposure of a weathering steel to the atmosphere with higher salt-content has been unclear.

It becomes evident that the mass fraction of the Cr-UFG and the Cr-goethite decreased and that of $\beta$-FeOOH increased in the higher salt content, as was shown in Fig.6. This indicates that the phase-transformation route from $\gamma$-FeOOH to the Cr-goethite reported before in a low salt-content atmosphere was swerved by the effect of chloride. Figure 8 shows the relative mass fractions of the goethite type phase including both the Cr-UFG and the Cr-goethite, $\beta$-FeOOH and $\gamma$-FeOOH in the rust layers on Steel B. Assuming that the initially formed rust was $\gamma$-FeOOH even in the higher salt content, the rust transformation routes during 17 years can be indicated by the arrows. It can be seen that all the rust layers are located in the goethite-rich region. However, it should be noted that angle between the arrow and the $\gamma$-FeOOH $\beta$-FeOOH line (the base line), $\theta$, decreases with increasing the salt content in the atmosphere. This means that the rust layer partly became to be on the $\gamma$-FeOOH to $\beta$-FeOOH transformation route in stead of the $\gamma$-FeOOH to the Cr-goethite route reported in a low salt-content environment. This $\gamma$-FeOOH to $\beta$-FeOOH transformation and resultant $\beta$-FeOOH forma
Fig 8 Relative mass fraction between the goethite type phase, $\beta$-FeOOH and $\gamma$-FeOOH on the surface of Steel B, evaluated by both X-ray diffraction and transmission Mössbauer spectroscopy.

Fig 9 shows the corrosion loss and $\beta/\alpha$, which was calculated from the X-ray diffraction results shown in Figs. 3 and 4. It seems that the corrosion loss is related to the $\beta/\alpha$. When $\beta/\alpha$ increases to more than about 0.5, the corrosion loss becomes higher. These results emphasize the significance of the transformation route of the rust layer towards the goethite type phase or $\beta$-FeOOH for discussing the protective ability of the rust layer in the environment with higher salt content.

5. CONCLUSION

The rust layers formed on low-alloy steels exposed for 17 years in various atmospheric environments with different salt content between 0.005-0.093 mgNaCl/100cm$^2$/day has been examined by using the X-ray diffraction and the Mössbauer spectroscopies.

It was found that the rust layers mainly consisted of the superparamagnetic ultra-fine Cr-goethite (Cr-UGF), the X-ray detectable Cr-goethite, $\beta$-FeOOH, and very small amount of $\gamma$-FeOOH and FeO$_2$.

Mass fraction of $\beta$-FeOOH increases with the salt content, therefore with increasing corrosion loss of the steels, whereas those of both of the Cr-UGF and the Cr-goethite showed their minimum at 0.04mdd. It was pointed out that increase in the mass fraction of $\beta$-FeOOH and decrease in that of the goethite type phase in higher atmospheric salt content cause the lower protective ability of the rust layer against the atmospheric corrosion.

These results emphasize the significance of the rust transformation route with time towards the goethite type phase or $\beta$-FeOOH for discussing the protective ability of the rust layer in the environment with higher salt content.

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